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+20°C from 250% to 500%, and a tear resistance  $R_a$  at +20°C of at least 9 daN/mm<sup>2</sup>, and in that the layer of plastics material is formed essentially of a polyurethane obtained by continuous reactive casting on a flat horizontal support of a reaction mixture of an isocyanate component and a polyol component, the isocyanate component comprising at least one aliphatic or cycloaliphatic di-isocyanate or a di-isocyanate prepolymer, this component having a viscosity measured at +40°C less than about 5 Pas, the isocyanate component containing urea functions, the content of urea being up to 10% of the total weight of isocyanate component, the urea content preferably being from 5 to 7%, and the polyol component comprising at least one long difunctional polyol of molecular weight from 500 to 4000 and at least one short polyol as a chain lengthening agent, the ratio of isocyanate group equivalents to hydroxyl group equivalents is about 1, and the proportions between the different polyols are selected so that the number of hydroxyl group equivalents due to the short diol represents from 20 to 70% of the total hydroxyl groups.

2. A laminated pane comprising only a glass sheet and a layer of transparent plastics material, characterised in that the layer of transparent plastics material has properties of absorption of energy and interior protection defined by a resistance to scratching greater than 20 g measured with the Erichsen type 413 apparatus and a resistance to abrasion according to European Standard R43 such that the difference in haze is less than 4% and, at a thickness of about 0.5 mm, a flow stress  $\sigma_y$  at -20°C not exceeding 3 daN/mm<sup>2</sup>, a stress at rupture  $\sigma_R$  at +20°C of at least 2 daN/mm<sup>2</sup>, a lengthening at rupture  $\epsilon_R$  at +20°C from 250 to 500%, and a tear resistance at +20°C of at least 9 daN/mm, and in that the layer of plastics material is formed essentially of a polyurethane obtained by continuous



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Form 10

PATENTS ACT 1952

# COMPLETE SPECIFICATION

(ORIGINAL)  
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TO BE COMPLETED BY APPLICANT  
SAINT-GOBAIN VITRAGE

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Complete Specification for the invention entitled: **"LAMINATED SAFETY PANE"**

The following statement is a full description of this invention, including the best method of performing it known to me:—

**Note** The description is to be typed in double spacing, size type 10cc, in an area not exceeding 220 mm in depth and 100 mm in width, on tough white paper of good quality and it is to be inserted inside this form.

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It has already been suggested for example in Patent Publications US-3 509 015 and US-3 808 077 to provide laminated panes comprising a glass sheet and a single layer of plastics material having properties of absorption of energy. This type of pane has not apparently given entire satisfaction, probably because of an insufficient resistance to abrasion and scratching of the layer of plastics material used as the external layer.

It is known in a general way that a structure of a laminated pane comprising a single layer of plastics material having simultaneously the properties of absorbing energy and a good resistance to scratching and to attack by exterior agents was unlikely to be satisfactory. In fact, for a man in the art there exists a certain incompatibility between the functions of absorbing energy and resistance to scratching for a single layer. For the layer to have properties of absorption of energy it is believed that it has to have an essentially thermoplastic character. On the other hand, for the layer to have a good resistance to scratching it is believed that it has to have an essentially thermohardening character with a cross-linked structure. These mechanical properties associated with thermoplastic or thermohardening characteristics are described for example in French Patent Publication 2398606 and European Patent Publication 0054191.

There has now been found a single layer of plastics material which, in a laminated pane structure in which it is associated with a glass sheet fulfills the function of absorbing energy, protection against fragments of glass and which also has a good resistance to abrasion and scratching and to different attacks from exterior agents.

35

~~The layer according to the invention is formed in a process which is continuous by reactive casting on a flat horizontal support from which it may be detached, of a~~



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by heating. This reactive casting which forms the layer having good mechanical and optical properties will be described more completely in the following description.

The proportions of components of the polyurethane are chosen  
5 to obtain preferably a balanced stoichiometric system, that  
is to say the ratio of equivalent NCO groups provided by the  
diisocyanate component to equivalent OH groups provided by  
the polyol component, that is to say the long polyol or poly-  
ols and the short diols is of the order of 1. When the ratio  
10 NCO/OH is less than 1, the more it decreases the more the  
desired mechanical properties for this application become  
less satisfactory. When all the components of the polyure-  
thane are difunctional the lower limit of the NCO/OH ratio  
for obtaining satisfactory mechanical properties is about  
15. 0.9. When one of the components at least is trifunctional  
this low limit may be lowered to about 0.8. When the ratio  
20. NCO/OH is greater than 1, the more it increases and the  
greater become certain mechanical properties of the layer  
obtained by reactive casting, for example the layer becoming  
more rigid, but given the higher cost of the isocyanate com-  
ponent with respect of that of the polyol component, the  
choice of a ratio NCO/OH substantially equal to 1 is a good  
compromise between the properties obtained and the cost.

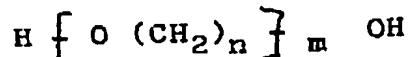
Suitable diisocyanates which may be used in the invention are  
25. chosen especially from the difunctional aliphatic isocyanates  
following: hexamethylenediisocyanate (HMDI), 2,2,4-trimethyl  
1,6-hexanediiisocyanate (TMDI), bis 4-isocyanatocyclohexylme-  
thane (Hylene W) bis 3-methyl-4-isocyanatocyclohexylmethane,  
30 2,2 bis (4-isocyanatocyclohexyl) propane, 3-isocyanatomethyl-  
3,5,5 trimethylcyclohexyl-isocyanate (IPDI), m-xylylenediiso-  
cyanate (XDI), m-and p-tetramethylxylylenedi-isocyanate (m-  
and p-TMXDI), trans-cyclohexane-1,4 diisocyanate (CHDI), and  
1,3 - (diisocyanatomethyl)-cyclohexane (hydrogenated XDI).



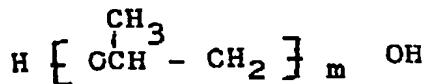
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preferably used 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate comprising urea functions (IPDI and derivatives thereof).

The long polyols which are suitable are chosen from polyether diols and polyester diols of molecular weight 500 to 4000; the polyesterdiols being products of esterification of a diacid such as adipic acid, succinic acid, palmitic acid, azelaic acid, sebacic acid, orthophthalic acid and a diol such as ethyleneglycol, propanediol -1,3, butanediol -1,4, hexanediol -1,6, and polyetherdiols of general formula



where n = 2 to 6; m is such that the molecular weight is situated in the range 500 to 4000, or polyether-diols of general formula:



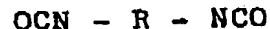
where m is such that the molecular weight is also situated in the range 500 to 4000. It is also possible to use polycaprolactonediols.

There is used preferably a polytetramethyleneglycol (n = 4) of molecular weight also equal to about 1000.

The lengthening agents for chains which may be used are the short diols such as ethyleneglycol, propanediol-1,2, propanediol-1,3, butanediol-1,2, -1,3 and -1,4, dimethyl-2,2-propanediol-1,3 (neopentylglycol), pentanediol-1,5, hexanediol-1,6, octanediol-1,8, decanediol-1,10, dodecanediol-1,12, cyclohexanedimethanol, bisphenol A, methyl-2 pentanediol-2,4, methyl-3 pentanediol- 2,4, ethyl- 2 hexane-diol-1,3, trimethyl-2,2,4-pantanediol-1,3, diethylene-glycol, triethyleneglycol, tetraethyleneglycol, butyne-2-diol-1,4, and substituted

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or



5 - R" - NH - CO - NH - R" -



biuret



15 In these operating conditions, even with difunctional components, when the NCO/OH ratio is substantially equal to or greater than 1, as indicated before, the product obtained is not completely thermoplastic; in fact it is infusible and insoluble in the majority of solvents for polyurethanes such as tetrahydrofuran and dimethylformamide. This does not present any disadvantage when the layer is already formed; on the contrary advantage is taken of the improved mechanical properties for the layer especially regarding the stress at the start of flow  $\gamma$ , the stress at rupture  $R$ , elongation at rupture  $R_e$ , the resistance to scratching measured in the ERIKSEN test as described below, or the resistance to abrasion, in comparison with an equivalent system polymerised at low temperature when only a linear polycondensation is produced.

When the NCO/OH ratio is less than 1 and of the order of 0.8 to 0.9, a reticulation of the type described above is produced only to an insignificant extent.

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Resistance to abrasion, with a difference in haze less than 4% measured according to the abrasion test indicated below.

5 According to one of the aspects of the invention, a part of the polyol component may be replaced by a different product having active hydrogens such as an amine.

10 According to another embodiment of the layer of plastics material according to the invention, the isocyanate component may contain within limited proportions, for example less than about 15% in NCO equivalents, at least one triisocyanate such as a isocyanate biuret or a triisocyanurate.

15 To fulfill all the functions which are demanded, the polyurethane layer according to the invention should have a thickness generally greater than 0.4mm and preferably greater than 0.5mm.

20 The layer according to the invention may contain various additives which generally serve to facilitate manufacture by reactive casting. It may contain a catalyst such as a tin catalyst for example tin dibutyldilaurate, tributyltin oxide, tin octoate, an organomercuric catalyst, for example mercuricphenylester, an amine catalyst such as for example diazabicyclo-(2,2,2)-octane, and 1,8-diazabicyclo (5,4,0)-1 decene-7. The layer may contain stabilisers such as bis (2,2,6,6-tetramethyl-4-piperidyl)sebacate, and a phenolic antioxidant.

25 The layer may also contain a spreading agent such as a silicone resin, a fluoroalkyl ester, or an acrylic ester.

30 Examples of manufacture of laminated panes and the layer of plastics material used for this manufacture are described in the following.

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To make the pane there is assembled a sheet of plastics material with a sheet of 2.6mm thickness of heated glass. The glass may possibly be hardened or tempered. This assembly may be carried out in two stages, a first stage consisting of a preliminary assembly obtained by passage of the elements forming the pane between two rollers of a calendar and it is possible to use for this purpose a device described in European Patent Publication 0015209, and a second stage consisting of putting the laminated product in an autoclave where, for about one hour it is subjected to a pressure of about 10 bars at a temperature of about 13°C. This autoclave cycle may possibly be replaced by a stoving cycle at normal pressure.

The pane obtained has an excellent optical quality and a perfect transparency.

The adhesion obtained between the glass sheet and the sheet of plastics material is measured by a peel test described below.

There is cut a strip of 5cm width from the covering layer. The end of the strip is unstuck and there is applied thereto a pulling force perpendicular to the surface of the glass at a pulling speed of 5 cm per minute. The operation is carried out at 20°C. There is noted the pulling force required for unsticking of the strip. Operating in this way there is obtained a pulling force of 10 daN/5cm.

Trials for resistance to shock at different temperatures are carried out on the pane made according to the example.

A first trial for resistance to shock is carried out at +20°C with a steel ball weighing 2.260 kg (heavy ball test) which is allowed to fall onto the central part of a square glass sample of 30.5 cm side, held on a rigid frame. There is determined the approximate height for

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The layer according to the example has a difference in haze of 0.94%.

5 The pane according to the example has all the characteristics which render it suitable for use as a vehicle windscreen.

Example 2

10 The procedure of Example 1 is followed except that the polyol component is formed of a mixture of polytetramethylene glycol of molecular weight 1000, butanediol-1,4 and polycaprolactonetriol (for example the product sold commercially under the name Niax 301 by UNION CARBIDE) in 15 respective proportions such that for one total hydroxyl equivalent, there is used 0.35, 0.45 and 0.20 hydroxyl equivalent.

20 There is made a layer of 0.70mm thickness. The pane obtained shows mechanical and optical characteristics which are completely satisfactory. The values measured in different tests are as follows:

25 - an adhesion of 11 daN/5cm, values of 8 metres with a heavy ball, 11 at 11 metres respectively with a light ball at -20°C and + 40°C.

a resistance to scratching of 35 g and a difference in haze on abrasion of 1.2%.

30 The pane made according to the example is thus suitable for use as a windscreen.

Example 3

35 The procedure of Example 2 is followed except that the proportions between the different polyols are such that for an equivalent total hydroxyl there is used 0.35, 0.55 and 0.10 hydroxyl equivalent respectively for the long

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The claims defining the invention are as follows:-

1. A laminated pane comprising only a glass sheet and a layer of transparent plastics material, characterised in that the layer of transparent plastics material has properties of absorption of energy and interior protection defined by a scratch resistance greater than 20 g measured with the Erichsen type 413 apparatus and an abrasion resistance according to European Standard R43 such that the haze difference is less than 4% and at a thickness of about 0.5 mm a flow stress  $\sigma_y$  at  $-20^\circ\text{C}$  not exceeding 3 daN/mm<sup>2</sup>, a rupture stress  $\sigma_R$  at  $+20^\circ\text{C}$  of at least 2 daN/mm<sup>2</sup>, a lengthening at rupture  $\epsilon_R$  at  $+20^\circ\text{C}$  from 250% to 500%, and a tear resistance  $R_a$  at  $+20^\circ\text{C}$  of at least 9 daN/mm<sup>2</sup>, and in that the layer of plastics material is formed essentially of a polyurethane obtained by continuous reactive casting on a flat horizontal support of a reaction mixture of an isocyanate component and a polyol component, the isocyanate component comprising at least one aliphatic or cycloaliphatic di-isocyanate or a di-isocyanate prepolymer, this component having a viscosity measured at  $+40^\circ\text{C}$  less than about 5 Pas, the isocyanate component containing urea functions, the content of urea being up to 10% of the total weight of isocyanate component, the urea content ~~preferably~~ being from 5 to 7%, and the polyol component comprising at least one long difunctional polyol of molecular weight from 500 to 4000 and at least one short polyol as a chain lengthening agent, the ratio of isocyanate group equivalents to hydroxyl group equivalents is about 1, and the proportions between the different polyols are selected so that the number of hydroxyl group



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3. A laminated pane according to claim 1 or 2, characterised in that the isocyanate component comprises 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate.

5 4. A laminated pane according to any one of claims 1 to 3, characterised in that the isocyanate component is formed essentially of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate having urea groups and in that the polyol component is formed essentially of polytetramethylene glycol and 1,4-butanediol.

10 5. A laminated pane according to one of claims 2 to 4, characterised in that the polyol of functionality greater than 2 is a polycaprolactonetriol.

15 6. A laminated pane according to one of claims 1 to 5, characterised in that for one equivalent of hydroxyl groups in total, the long polyol represents 0.30 to 0.45 equivalent, the short diol 0.2 to 0.7 equivalent and the 20 polyol of functionality greater than 2 0 to 0.35 equivalent.

25 7. A laminated pane according to one of claims 1 to 6, characterised in that the polyurethane layer having properties of absorption of energy and interior protection comprises additives such as a catalyst, a spreading agent and a stabiliser.

30 8. A laminated pane according to any one of claims 1 to 7, characterised in that the layer of transparent plastics material is obtained by reactive casting using a polymerisation temperature <sup>from 100°C to 140°C</sup> ~~greater than 90°C~~.



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